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# International Research Center for Elements Science – Organic Main Group Chemistry –

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## Scope of Research

Our research focuses on the development of new molecular transformations to improve or achieve ideal synthesis of functional molecules as well as to allow exploitation of new chemical (metal and carbon) resources. The present research subjects are: 1) metal-catalyzed carbon-carbon and carbon-heteroatom bond-forming reactions using universal metals such as iron; 2) development of smart materials based on the synergistic effect of various metals on artificial peptides; 3) development of smart metallic nanoparticle catalysts based on supramolecular approaches; and 4) understanding of reaction mechanism of these catalytic reactions with the help of quantum chemical methods and synchrotron X-ray absorption spectroscopy.



## KEYWORDS

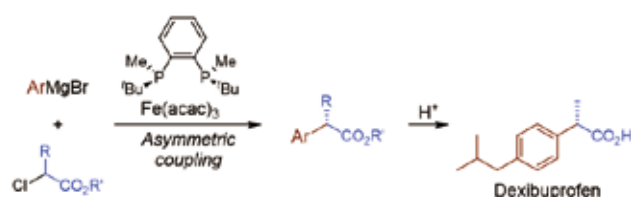
Selective Organic Reaction   Iron Catalyst   Metalated Peptide Catalyst   Metallic Nanoparticle Catalyst   Organic Synthesis

## Selected Publications

- Kawamura, S.; Agata, R.; Nakamura, M., Regio- and Stereoselective Multisubstituted Olefin Synthesis via Hydro/carboalumination of Alkynes and Subsequent Iron-catalysed Cross-coupling Reaction with Alkyl Halides, *Org. Chem. Front.*, **2**, 1053-1058 (2015).
- Jin, M.; Adak, L.; Nakamura, M., Iron-Catalyzed Enantioselective Cross-Coupling Reactions of  $\alpha$ -Chloroesters with Aryl Grignard Reagents, *J. Am. Chem. Soc.*, **137**, 7128-7134 (2015).
- Agata, R.; Iwamoto, T.; Nakagawa, N.; Isozaki, K.; Hatakeyama, T.; Takaya, H.; Nakamura, M., Iron Fluoride/N-Heterocyclic Carbene Catalyzed Cross Coupling between Deactivated Aryl Chlorides and Alkyl Grignard Reagents with or without  $\beta$ -Hydrogens, *Synthesis*, **47**, 1733-1740 (2015).
- Nakagawa, N.; Hatakeyama, T.; Nakamura, M., Iron-Catalyzed Suzuki-Miyaura Coupling Reaction of Unactivated Alkyl Halides with Lithium Alkynylborates, *Chem. Lett.*, **44**, 486-488 (2015).
- Nakagawa, N.; Hatakeyama, T.; Nakamura, M., Iron-Catalyzed Diboration and Carboboration of Alkynes, *Chem. Eur. J.*, **21**, 4257-4261 (2015).
- Takaya, H.; Nakajima, S.; Nakagawa, N.; Isozaki, K.; Iwamoto, T.; Imayoshi, R.; Gower, N.; Adak, L.; Hatakeyama, T.; Honma, T.; Takagi, M.; Sunada, Y.; Nagashima, H.; Hashizume, D.; Takahashi, O.; Nakamura, M., Investigation of Organoiron Catalysis in Kumada-Tamao-Corriu-Type Cross-Coupling Reaction Assisted by Solution-Phase X-ray Absorption Spectroscopy, *Bull. Chem. Soc. Jpn.*, **88**, 410-418 (2015).

## Iron-catalyzed Enantioselective Cross-Coupling Reactions of Alkyl Halides with Aryl Grignard Reagents

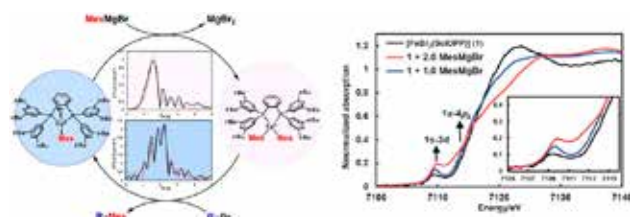
Transition-metal-catalyzed enantioselective cross-coupling reactions are powerful tools in the asymmetric synthesis of functional chiral molecules. Recently, we developed the first iron-catalyzed enantioselective cross-coupling reaction. The present reaction provides easy access to a variety of chiral  $\alpha$ -aryl esters, which are easily converted to important pharmaceutical compounds such as ibuprofen and naproxen.



**Figure 1.** Iron-catalyzed enantioselective cross-coupling reaction of  $\alpha$ -chloroesters with aryl Grignard reagents.

## Characterization of Solution-phase Organoiron Catalyst by Synchrotron X-ray Absorption Spectroscopy

In the past few decades, iron catalysts have regained much attention in cross-coupling chemistry due to their unprecedented reactivity and practical advantages. However, understanding of their mechanisms remains limited because characterization of organoiron intermediates has been hampered by their paramagnetic character and instability toward air and moisture. Recently, we discovered *in situ* XAFS analysis to be a feasible method to characterize iron intermediates in solution. The methods would also provide valuable mechanistic insight for a variety of transition-metal catalyses as well as iron catalysis. Now, we are trying to clarify the mechanism of several metal-catalyzed reactions by XAFS analysis to investigate effective catalysts and novel reactions.



**Figure 2.** Reaction mechanism of iron-catalyzed KTC-coupling of an arylmagnesium halide with an alkylhalide and the Fe K-edge XAFS spectra of organoiron intermediates.

## Supramolecular Approach for Creating Enhanced Catalysis of Metallic Nanoparticles

This project focuses on the development of highly active and selective metallic nanoparticle and cluster catalysts. To achieve this purpose, four key methodologies have been developed: 1) creation of reaction field with advanced self-assembly, 2) design of selective molecular transformation with multi-point intermolecular interaction, 3) size-selective synthesis of metallic nanoparticles and clusters, and 4) utilization of plasmonic resonance with light.

